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## Centers of Polymer Research; Polymer Science in Hokkaido, Japan

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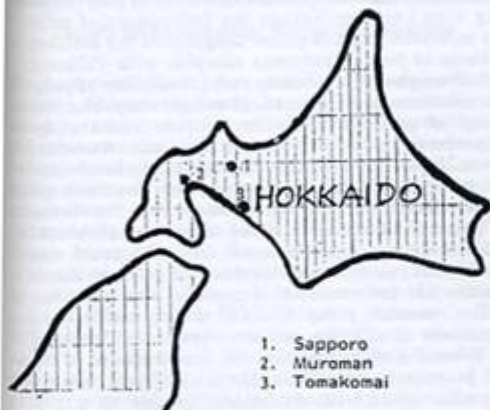
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Centers of Polymer Research

# Polymer Science in Hokkaido, Japan

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Hokkaido, The most northern and the second largest of the four major islands of Japan, is separated from Honshu, the main island of Japan, by the Tsugaru Straits. Tohoku-chiho, the north-eastern district of Honshu, has been a part of Japan since before the 10th. century, but Hokkaido, only 30 km away, was essentially uninhabited until the late 18th. century except for narrow regions along the coast. It was at this time that representatives of several major world powers explored the northern Pacific. Systematic exploration and settling of Hokkaido by Japan began after the middle of the 19th. century, in coordination with the modernization of Japan; thus, the historical background of Hokkaido is quite different from that of the rest of Japan. Hokkaido is the second largest island with a population of about seven million, but the population density is much less than that of any other part of Japan. The climate of this island is also different; there is no rainy season and the winters may be quite cold; Hokkaido has often been compared with New England in the United States. The capital of Hokkaido is Sapporo with a population of about 1.4 million.

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Junkichi Sohma

## HOKKAIDO UNIVERSITY

Hokkaido University, located in Sapporo, is the oldest university in Japan, although Hokkaido itself was settled only 100 years ago and in 1976 the university celebrated its centennial. Hokkaido University was founded as a College of Agriculture at the very beginning of the settling of Hokkaido and is now one of the largest national universities in Japan. The history is similar to many state (land grant) universities in the United States. When the agricultural college in Hokkaido was planned, a former dean of the University of Massachusetts, Prof. William S. Clark, was invited as an advisor and he became one of the founders of Hokkaido University. Today many visitors and specialists from the States, especially from New England, find similarities between their own homeland and Hokkaido, not only in vegetation but also in the style of housing. Visitors are made very welcome in Hokkaido. Education in Hokkaido, especially in polymer science is conducted at the national universities which are supported by the Ministry of Education of the Japanese Government.

Polymer research at Hokkaido University is carried out in four departments: the Department of Polymer Science, in the Faculty of Science; the Departments of Applied Physics, of Chemical Process Engineering, and of Applied Chemistry, in the Faculty of Engineering.

## Faculty of Science

*Department of Polymer Science:* This department consists of five research groups: Physics on Solid Polymers, Physics on Polymer Solutions, Polymer Physical Chemistry, Polymer Chemistry and Biopolymers. Professor Kunio Hikichi is conducting research on physics of solid polymers and is studying the physical properties of polypeptides in the solid state as well as in solution. In the solid state research, his emphasis is on the





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understanding of specific correlation between relaxation phenomena and the characteristic structure of synthetic polypeptides which have flexible side chains and rigid  $\alpha$ -helix backbone. With Associate Professor Akihiro Tsutsumi, synthetic polypeptides, polyglutamates and copolypeptides are investigated by broad-line nuclear magnetic resonance, dielectric and dynamic mechanical measurements, and spin-probe techniques to see the effect of intra- and intermolecular interactions on molecular motions. By x-ray diffraction and infrared absorption spectroscopy and molecular relaxation, it was found that  $\alpha$ -helices of polypeptides have the character of two phase systems. Research interest is also developing into biological materials such as collagen, keratin and milk-casein. With Associate Professor Tsutsumi and Instructor Toshifumi Hiraoki, Professor Hikichi is studying molecular dynamics of polypeptides and biomaterials in solution by high-resolution nuclear magnetic resonance and electron spin resonance. Studies are underway to evaluate, by  $^1\text{H}$  and  $^{13}\text{C}$  magnetic relaxations in aqueous solutions, the interaction of polypeptides and biomaterials such as polyglutamic acid, polyornithine, polylysine, chondroitin sulfate, carnosin, with paramagnetic metal ions; nuclear magnetic resonance studies on molecular stabilities and dynamical properties of Ca-binding proteins on parvalbumin, studies of molecular conformations and internal motions in oligo- and polypeptides by nuclear magnetic resonance, studies of molecular orientation and dynamical properties in polypeptides by electron spin resonance with spin-labeling technique are also being carried out.

Professor Tsurutaro Nakagawa is active in polymer physical chemistry and colloids and has made important contributions to the development of rheology in Japan. With Instructor Kunio Nakamura, he is now elucidating the mechanism of plasticization and "anti-plasticization" of polymers. Other subjects which are studied in cooperation with Associate Professor Tsuyoshi Komatsu and Instructor Masao Sakurai, are in the field of physical chemistry of hydrophilic colloids and polymers. Viscometric and conductometric studies of polyelectrolytes including polystyrene sulfonates, polyacrylates and polymethacrylates are being studied as is the interaction between heavy metals and polyelectrolytes by using potentiometric titration methods. Viscometry,

equilibrium dialysis, densitometry, sound velocity measurement, and ESR on some polysoaps and simple soaps are being carried out, including surface-chemical studies of soap-polymer interaction and ESR studies of molecular motion in soap micelles. The viscous drag reduction brought about in the turbulent flow by addition of a very small amount of polyoxyethylene is also being investigated.

Professor Motozo Kaneko is studying the thermodynamics and dynamic properties of polymer solutions. With Associate Professor Yasuhiro Miyake, Lecturer Mitsuo Nakata and Instructor Yoshinobu Izumi, he is concerned with the phase diagram of polystyrene, polyethylene and poly(ethylene glycol) solutions in several solvents especially the pressure effect on the upper and the lower critical solution temperature. He is also investigating with Lecturer Nakata the free energy of polystyrene solutions and the phase diagram of the solution of mixtures of two polystyrene samples with different molecular weights; the osmotic compressibility of polystyrene solutions near the critical temperature, the conformation of polysaccharide in solution and the dynamic properties of polyelectrolyte solutions. Associate Professor Miyake is investigating the chain conformation of macromolecules in solution and the dynamic critical phenomena of polymer solutions and the viscosities of polymer solutions near the critical temperature.

Until a few years ago, Professor Junzo Noguchi was responsible for research and teaching of polymer chemistry; since his retirement this position has not been filled. The research group has had a long tradition in the synthesis of silk-like protein. Associate Professor Seiichi Tokura is studying chemical modifications of the natural polysaccharide chitin. He is also investigating poly- $\alpha$ -amino acids with sulfhydryl groups as a SH-enzyme model. Lecturer Takashi Komai is interested in biomedical polymers and antithrombogenic membranes based on modified natural polysaccharides and poly- $\alpha$ -amino acids. Instructor Norio Nishi is synthesizing sequential polypeptides and enzyme model using cyclic peptides for the purpose of investigating the stereospecificity of the enzymes.

Professor Shintaro Sugai is exploring with Dr. Kunihiro Kuwajima the chain folding of small protein, such as  $\alpha$ -lactalbumin, and lysozyme, especially the transitions among the three states, the native, the intermediate and the denatured. With Instructor Katsutoshi Nitta, folding processes of ribosomal RNAs in eukaryotic cell are under investigation. Associate Professor Michio Yoneyama is conducting studies on hydrolysis and on the structures of the active sites of such enzymes as cellulase and lactase. Another area investigated by Professor Sugai is transitions of hydrophobic polyelectrolytes such as maleic acid-styrene copolymer for transitions of proteins.

#### Faculty of Engineering

*Department of Applied Physics:* Two research groups are interested in polymer research.

Professor Akira Odajima is investigating the structure of solid polymers by x-ray diffraction in combination with theoretical studies of the lattice dynamics and





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the paracrystal model for crystalline polymers. With Instructor Shigeru Yamane, by means of neutron spectroscopy and x-ray diffraction, they are investigating the microstructure of crystalline polymers produced by radiation-induced polymerization and the loss of crystallinity polymers by  $\gamma$ -irradiation with heavy dose, in cooperation with research groups in Tokai and the Takasaki Laboratories (with Dr. Osamu Yoda) of the Japan Atomic Energy Research Institute (JAERI). He is also interested in the oxidation of polymers induced by  $\gamma$ -irradiation. Research on ferroelectric polymers, polyvinylidene fluoride (PVDF) in the  $\beta$ -phase, by x-ray diffraction has uncovered the switching mechanism under an electric field. With Lecturer Keiji Tanaka and Instructor Tokihiro Ueno, physical properties of inorganic polymeric materials induced by photoillumination and photo-enhanced crystallization of amorphous selenium are under investigation. These phenomena have potential use for optical signal processing, switching and memory.

Professor Teruo Hideshima and his research group are studying relaxation spectroscopy of various polymers by means of dielectric, mechanical and broadband NMR measurements. With Lecturer Takuo Kakudate and Instructor Maeko Kakizaki, he is determining relaxation spectra for the loss bands found in linear and branched polyethylenes in the temperature range from  $-180^{\circ}\text{C}$  to the melting point. Professor Hideshima and Instructor Kakizaki are also investigating by creep and absorption current measurements, the retardation spectra of the side chain of methacrylate polymers and poly- $\gamma$ -n-alkyl-L-glutamate. From dielectric and mechanical data it is apparent that the spectral shapes are little affected by side chain length and conformation of the main chain.

*Department of Chemical Process Engineering:* This department provides an interdisciplinary curriculum between chemistry and chemical engineering.

Professor Yoshiyuki Takada is working now on polymer syntheses. With Associate Professor Kazuaki Yokota, Instructors Toyoji Kakuchi and Kazumi Yamaguchi, they are studying cyclopolymerization in the presence of alkylaluminum chlorides which leads to cyclized polymers of 9-20-membered rings and a polydentate ligand.

With diethylaluminum chloride, the preferential production of oligomers of the methacrylate was observed. In addition, the preparation and the properties of photo-reactive polymers, and the preparation of ion-containing polymers by polyaddition are also being studied.

Professor Junkichi Sohma is broadly interested in application of magnetic resonances, ESR and NMR, to the investigation of polymers. His research activity is divided into two areas—studies of molecular motions of polymers and mechanochemistry of polymers. With Instructor Masaru Shiotani, he carried out spin-label experiments by using ESR with spin-labeling technique to detect selectively the localized motion of the side chain in solid PMMA as well as in benzene solution. Anisotropy of molecular motion of the side chains is quantitatively determined. A new ESR technique, the Saturation Transfer apparatus, is now being developed by Associate Professor Keiichi Ohno, and will be applied to the study of molecular motion of polymers. Deuterium NMR is being used to determine partial orientation and molecular motions of side chain of poly-(benzyl glutamate) in concentrated benzene solution. Scissions of polymer main chains by mechanical fracture of solid polymers have been demonstrated by ESR. Professor Sohma and Instructor Masayoshi Tabata are now exploring various aspects of mechanochemistry of polymers by NMR, molecular mechanism for polymer fractures, structure changes induced by fracture in crystalline polymers, and chemical reactions initiated by mechanical agitations. Another area of research of this group is the application of high resolution NMR for solid samples to detect crosslinks induced by  $\gamma$ -irradiation into solid polymers.

*Department of Applied Chemistry:* Professor Jisuke Hayashi is interested in the detailed analysis of structures of various kinds of cellulose by x-ray diffraction. The main subjects of studies of his group, which includes Associate Professor Kunio Tosaka, Instructor Mitsuo Takai, are crystalline and supermolecular structure of cellulose and pulping and refining of wood and nonwood materials. They are interested in the chain conformations of cellulose I and II, the transformation of cellulose I to II and modifications from cellulose I to the cellulose II family. A mechanism of spontaneous association and crystallization of the preformed glucans for the formation of cellulose microfibril is being developed. Studies by polarizing microscopy indicate that cellulose microfibrils in the spherulites of bacterial cellulose from different strains are oriented radically or tangentially. More recently, Professor Hayashi in cooperation with Instructor Mitsuo Takai has become interested in the biochemical studies and bioenergy, the chemical and enzymatical saccharification of plants and cellulosic waste materials.

## MURORAN INSTITUTE OF TECHNOLOGY, MURORAN

Muroran is the largest port in Hokkaido and one of the largest industrial areas on this island. Muroran Institute of Technology was established as Muroran Technical College in 1939 and transformed into an institution of university level in 1949; it has a single fac-

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ulty consisting of 11 departments.

Professor Fujio Komatsu has interest in polymer blends and is investigating, in cooperation with Instructor Takayoshi Shoji, melt viscosity and viscoelastic behavior; they are also trying to use ash originating from the eruptions of the near-by active volcano, Mt. Usu, as materials to reinforce polymers. Professor Noboru Nishida is interested in relaxation phenomena of polymers particularly of concentrated polyelectrolyte solutions; he also is relating the rheological properties with the molecular weight distribution of polyisobutylene.

### **TOMAKOMAI TECHNICAL COLLEGE, TOMAKOMAI**

Tomakomai Technical College is situated in the city of Tomakomai, a rapidly developing industrial city in

Hokkaido. The college was founded in 1965 and is specializing in engineering.

Professor Motoh Yoshida is interested in electrical phenomena of polymer films and the transfer of electric charges induced by the contact of polymer films with metals or other polymers. The decay of the electric charges or electric current due to relaxation of the charges injected into the polymer films are being measured in order to elucidate the mechanisms of electric charge transfer.

Associate Professor Kikuya Kimura is working on cellulose chemistry, the decrease of crystallinity in cellulose, and its relation to the degree of polymerization, the effect of grinding on cellulose and the comparison of structures, and crystalline transitions of cellulose as a function of decrease of crystallinity by mechanical treatment of cellulose.